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(54) Title: TREATMENT OF FIBRE			
(57) Abstract  Regenerated cellulose fibre with a reduced tendency to fibrillation can be prepared by treating never-dried fibre with an aqueous solution or dispersion of a polymer having a plurality of cationic ionisable groups. Suitable polymers include those carrying imidazoline and azetidinium groups. The fibre may additionally be treated with an aqueous emulsion of an emulsifiable polymer.			

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### Treatment of Fibre

#### Technical Field

This invention relates to the treatment of fibre and has particular relevance to the treatment of solvent-spun regenerated cellulose fibre.

#### Background Art

Proposals have been made to produce regenerated cellulose fibre by spinning a solution of cellulose in a suitable solvent. An example of such a process is described 10 in UK Patent Specification 2043525, the contents of which are incorporated herein by way of reference. In such a solvent spinning process, cellulose is dissolved in a solvent such as a tertiary amine N-oxide, e.g. N-methylmorpholine N-oxide, which is a solvent for the 15 cellulose. The solution is then spun through a suitable die to produce filaments, which are washed in water to remove the solvent. The fibres may be stretched during the processing, both before and after washing as required. Typically, the fibre is then treated with a finish before 20 being utilised in a known manner.

The present invention is particularly concerned with the treatment of such solvent-spun cellulose fibre so as to reduce the tendency of the fibre to fibrillate. Fibrillation is the breaking up in a longitudinal mode of the fibre to 25 form a hairy structure. A practical process to reduce fibrillation needs not only to reduce fibrillation itself, but also to have a minimal effect on subsequent dyeability of the fibre and to have as little effect as possible on tenacity and extensibility of the fibre. Processes have been 30 investigated which will reduce fibrillation but these unfortunately reduce the tenacity and the extensibility of the fibre. Other processes have been investigated which, while not reducing tenacity and extensibility, have a deleterious effect on the dyeability of the fibre.

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which not only reduces fibrillation tendency but also yields a treated fibre which has a significantly reduced tendency to fibrillate without significant reduction in tenacity and extensibility and without significant deleterious effect on 5 dyeability. Maintaining a balance between all of the required properties of the fibre is extremely difficult because it is not sufficient to produce a fibre with a low tendency to fibrillation but which has a very low tenacity or a very low extensibility or a very poor dyeability. It 10 would also be unsatisfactory to produce a fibre which was so rigid as to be unworkable or so embrittled as to be unprocessable.

Disclosure of Invention

A method according to the invention of manufacturing 15 regenerated cellulose fibre with a reduced tendency to fibrillation is characterised in that never-dried regenerated cellulose fibre is treated with an aqueous solution or dispersion of a polymer having a plurality of cationic ionisable sites. Never-dried fibre is regenerated 20 fibre which has been washed after regeneration in preparation for drying but which has not yet been dried. Never-dried fibre has different physical properties from fibre which has been dried and rewetted; for example it generally has a higher water imbibition.

25 A regenerated cellulose fibre according to the invention is characterised in that it bears a coating which comprises a polymer having a plurality of cationic ionisable sites. The coating may optionally comprise in addition an emulsifiable polymer.

30 The regenerated cellulose fibre according to the invention is preferably a solvent-spun fibre prepared by a method including the steps of:

- (i) dissolving cellulose in a water-miscible solvent to form a dope;

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- (ii) extruding the dope to form extruded filaments;
- (iii) passing the extruded filaments into water to remove solvent and form regenerated cellulose fibre;
- (iv) treating the resulting wet fibre in never-dried state with an aqueous solution or dispersion of a polymer according to the method of the invention; and
- 5 (v) drying the resulting treated fibre.

The wet fibre is optionally treated in addition with an aqueous emulsion of an emulsifiable polymer so as to exhaust the emulsifiable polymer onto the wet fibre. The wet fibre may be treated with a mixture of water-soluble or water-dispersible polymer having a plurality of cationic ionisable sites (herein "polyelectrolyte") and aqueous emulsion of emulsifiable polymer. The mixture may further include glyoxal as a cross-linking agent. The mixture may further include a catalyst to enhance the cross-linking of the glyoxal.

Typically the fibre is treated to give a total of 0.1 to 1.0% solids by weight of dry fibre on the fibre. The weight of solids may be in the range 0.2 to 0.8% or 0.3 to 0.6% or 0.4 to 0.5%, based on dry fibre.

The fibre may be treated by padding, in which the fibre is brought into contact with a surface carrying the treatment solution, or by immersion and exhaustion.

The fibre may be treated with conventional finishes between the step of passing into water to remove solvent and the treatment with the polyelectrolyte or after that treatment.

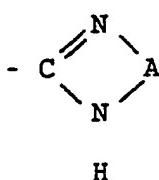
30 When an emulsifiable polymer is used, the polyelectrolyte and the emulsifiable polymer may be mixed together for simultaneous treatment of the cellulosic fibrous material, or the cellulosic material may be first

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treated with the polyelectrolyte and then treated with the emulsifiable polymer.

A preferred class of polyelectrolytes is that comprising polymers (e.g. having a molecular weight of from 5 20,000 to 10,000,000 viscosity average) having a backbone exclusively of carbon atoms to which are attached units of the formula:

10



where A is a C<sub>2</sub> to C<sub>3</sub> alkylene group in which different carbon atoms are linked to the two nitrogen atoms. Such polymers may be prepared by reacting a di- or poly-amine 15 with a polymer of a nitrile-group-containing monomer. When A is a C<sub>2</sub> alkylene group the units are imidazoline units. A particularly preferred polyelectrolyte of this class is that sold under the Trade Mark "Primafloc C7", which is believed to be a poly(vinylimidazoline) in the class just 20 described. Alternatively, polyelectrolytes based on polyacrylamides or water soluble polyamides may be used.

A particularly preferred class of polyelectrolytes is that in which at least some of the cationic ionisable sites are azetidinium cations. Such sites can be formed by 25 reaction of a secondary amine group with an epihalohydrin, for example epichlorhydrin. Polymers containing secondary amine groups can be prepared for example by condensation of a diacid, for example adipic acid, with a compound which contains two primary amine groups and at least one secondary 30 amine group, for example diethylenetriamine. Such a condensation yields a polyamide containing secondary amine groups. One suitable polymer having a plurality of cationic ionisable sites of this class is sold by Hercules Powder Corporation under the Trade Mark "Hercosett 125". Another

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suitable polymer is sold by the Stephenson Group under the Trade Mark "Listrilan SR".

The use of polymers which incorporate azetidinium cations, in particular Hercosett 125, as dyeing aids for 5 cotton is described by S.M. Burkinshaw et al. in Journal of the Society of Dyers and Colourists, Volume 105 (1989), pages 391-398, and Volume 106 (1990), pages 307-315. Although it was noted that the use of such dyeing aids did not significantly affect the tensile properties of cotton 10 fabrics, there was no suggestion that such use might have any effect on the properties of the fibres, in particular their tendency to fibrillate. Cotton fibres indeed have little tendency to fibrillate. This may be related to the fact that they have a complex morphology based on the 15 cellulose I structure, whereas solvent-spun regenerated cellulose fibres have a relatively simple morphology based on the cellulose II structure. There is furthermore no suggestion that such polymers would be of value when applied to never-dried regenerated cellulose fibres, rather than to 20 cotton fibres immediately prior to dyeing.

A wide variety of polymers may be used as the optional emulsifiable polymer in the method of the invention, the essential requirement simply being that the polymer should be emulsifiable in water. Suitable polymers include 25 polyacrylates, polyvinyl acetates and copolymers of vinyl acetate, polyolefins and particularly polyethylenes. Polyethylene emulsions sold under the Trade Mark "Bradsyn P.E." (Hickson & Welch), under the Trade Mark "Iberlene P.E." (Harrison Chemicals), under the Trade Mark "Mykon SF" 30 (Warwick Chemicals), vinyl acetate copolymer emulsions sold under the Trade Marks "Vinamul 6000 and "Vinamul 6515" (Vinyl Products) and polyvinyl acetate emulsion sold under the Trade Mark "Calatac VB" (I.C.I.) may be used. In the case of polyethylene emulsions, the polymer should 35 preferably have a melting point of about 100-105°C, a molecular weight below about 5000, an acid number of under

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20 and a carbonyl content of not more than 1% >C=O by weight.

An emulsifying agent is often necessary to emulsify the polymer, and a nitrogen-free non-ionic emulsifying agent 5 such as poly(ethylenoxyalkylphenol) may be used.

The aqueous polymer emulsion may be cationic, non-ionic or anionic, but a non-ionic polymer emulsion may be preferred.

The pH of the emulsion may be in the range 4 to 7, 10 particularly from 5 to 6. The emulsion should be rather dilute, and will generally contain considerably less than 1% by weight solids. Under favourable conditions, exhaustion is rapid and complete; completion of the process can be readily observed because the liquor, which is initially turbid, 15 becomes completely clear after the fibre has been immersed in the treatment liquor.

Temperatures in the range 20°C to 60°C, e.g. 25°C to 30°C, are preferred as treatment temperatures.

The concentrations of the polyelectrolyte and of the 20 optional emulsifiable polymer in the treatment liquor are chosen having regard to the amount of solids desired on the fibre and to the type of equipment to be used for the treatment. The concentration of polymer solids in the treatment liquor may for example be 1-25 g/l, more 25 preferably 5-20 g/l, most preferably 10-15 g/l. The treatment bath may optionally also contain a crosslinking agent such as glyoxal. When used, the crosslinking agent is preferably present in the bath at a concentration of 2 to 10 g/l, more preferably 4 to 8 g/l. The treatment bath may 30 additionally contain a catalyst for the crosslinking reaction, for example that sold by BASF under the Trade Mark "Condensol FB".

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The amount of polyelectrolyte deposited onto the fibre may be from 0.05% to 1.0%, preferably 0.1% to 0.5%, by weight on the weight of the fibre. When used, the amount of emulsifiable polymer that is exhausted onto the fibre may be 5 from 0.1% to 4.0%, preferably 0.75% to 2.0%, by weight.

The term "exhaustion" has been used to describe the transfer of disperse phase particles from an emulsion or suspension (without breaking the emulsion or suspension) to the fibre immersed in it or to which the emulsion is 10 applied; it is not intended to imply that the process must necessarily be complete (i.e. that the supply of the disperse phase particles must necessarily be exhausted) although complete exhaustion will generally be convenient in batch operation in providing automatic control over the 15 amount of polymer deposited.

After exhaustion has taken place, excess liquor is removed from the treated fibre by hydroextraction, for example by centrifuging or mangling, and the regenerated cellulosic fibre is then dried, preferably at a temperature 20 of about 80-100°C.

When the process of this invention is performed as a batch operation, the fibres are simply immersed in the treatment bath or baths containing the treatment liquors. The liquor to fibre ratio in the bath is in no way critical 25 to the invention. Liquor to fibre ratios of from 5:1 to 100:1, e.g. 30:1, may be found convenient.

Alternatively, the process may be carried out continuously on a continuous length of fibre. The continuous treatment may best be carried out using a pad mangle, 30 although application may be made from baths of a conventional backwasher. In either case it is essential that during or after the impregnation step, a sufficient degree of exhaustion of polymer onto the fibre to reduce the fibrillation tendency should occur before the treated goods

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are subjected to further stages of processing, e.g. rinsing, treating with other agents or drying. The time for the exhaustion to occur will depend both on the mixture of the polymer and the properties of the fibre being treated, but 5 should not normally exceed 15 minutes. The exact times and conditions may readily be determined by experiment.

When the regenerated cellulose fibre is a solvent-spun fibre, the solvent is preferably a tertiary amine N-oxide and is further preferably N-methylmorpholine N-oxide.

#### 10 Brief Description of Drawings

By way of example, embodiments of the present invention will now be described with reference to the accompanying drawings, of which:-

Figure 1 is a graph of Fibrillation Index (F.I.) 15 against concentration, and

Figure 2 is a graph of tenacity and extensibility against treatment bath concentration.

It will be appreciated that the method described in this specification is somewhat similar to the process 20 described in British Patent Specification 1340859 which specification describes a process for treating wool in order to render it shrink-resistant. It is not known why a process for treating wool to render it shrink resistant should be suitable for treating never-dried regenerated cellulose 25 fibre to render it resistant to fibrillation whilst still permitting the cellulose fibres to retain adequate tenacity extensibility and dyeability. It will further be appreciated that there are vast numbers of processes for the treatment of fibres in existence and it is not practical or 30 possible to predict the effects of the treatment of a proteinaceous fibre such as wool when compared to a regenerated cellulosic fibre such as solvent spun regenerated cellulose.

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Example 1-12

To carry out a series of tests, a plurality of cellulose strands were extruded from a solution of cellulose in N-methylmorpholine N-oxide and passed into a water bath 5 to remove the solvent. The fibre thus produced was then passed through one of a number of treatment baths having a variety of chemical compositions (Baths 1-12) and through a spin-finish bath to apply conventional spin-finishes.

Details of the treatment bath contents, which 10 incorporate an essential element of the invention, are given below.

The cellulosic fibre treated with different treatment baths was then processed into yarn by conventional spinning techniques, and subsequently yarn samples were dyed on a 15 small scale by a process which simulates large scale dyeing.

The details of the dyeing of the fibre samples were as follows:-

2 g of fibre was first placed in a stainless steel cylinder approximately 25 cm high by 4 cm diameter. The 20 cylinder had a capacity of approximately 250 ml, and at each step in the treatment 50 ml of solution was added to the 2 g of fibre.

The first step was to scour the fibre to remove the spinning lubricant. A conventional scouring solution of 25 anionic detergent and  $\text{Na}_2\text{CO}_3$  at 94°C was added to the fibre, a screw cap was applied, and the capped cylinder was tumbled end over end for 45 minutes at about 60 tumbles per minute.

The scouring solution was then removed, and the fibres were washed in water and bleached for 1 hour at 95°C. Again 30 the cylinder was capped and tumbled at 60 tumbles per

- 10 -

minute.

The bleaching solution used contained:-

7.5 cc/litre H<sub>2</sub>O<sub>2</sub> (at 35% concentration)

1 g/l NaOH

5 1 g/l of a peroxide stabiliser and heavy metal sequestrant ("Contivan SNT" available from CHT Products Limited)

After bleaching, the fibres were washed and dyed using 4% Procion Navy HER 150 reactive dye ("Procion" is a Trade 10 Mark of Imperial Chemical Industries plc). Dyeing took place at 80°C in the capped cylinder in an aqueous solution containing 80 g/l NaCl and 20 g/l Na<sub>2</sub>CO<sub>3</sub>. Again the cylinder was tumbled end over end at 60 tumbles per minute.

After dyeing, the fibres were washed and dried. The 15 fibres were then assessed for the amount of fibrillation, the dyeability of the fibre, fibre tenacity, fibre extensibility and water imbibition.

To measure the fibrillation and to fix a scale so that changes in fibrillation could be determined, a series of 20 fibres having a range of degree of fibrillation from zero upwards was identified. A standard length of fibre was then taken and the number of fibrils (fine hairy spurs extending from the main body of the fibre) along the standard length was counted. The length of each fibril was measured, and an 25 arbitrary number, being the product of the number of fibrils multiplied by the average length of each fibril, was determined for each fibre. The fibre in this series having the highest such number was then identified as the most fibrillated fibre and was assigned the arbitrary 30 Fibrillation Index of 10. The wholly unfibrillated fibre was assigned a Fibrillation Index of zero, and the remaining fibres were evenly ranged from 1 to 10 based on the microscopically measured arbitrary numbers. As a guide, the fibrils on a fibre having Fibrillation Index 1 are just

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visible to the eye.

The measured fibres were then used to establish an optical scale. To determine the Fibrillation Index for any other fibres, a sample of five or ten fibres was visually compared under the microscope with the set of graded fibres. 5 The visually determined numbers were then averaged to give a Fibrillation Index for fibres having received a given treatment. It will be appreciated that visual comparison and averaging is many times quicker than measurement, and it 10 has been found that skilled fibre technologists are consistent in their rating of the fibres.

Tenacity (in centinewton/tex) and extensibility (in per cent) were measured using conventional equipment, and again measurements were made on several fibres (usually ten) and 15 the arithmetic mean calculated.

Dyeability was determined by visual comparison.

Solvent-spun cellulose not treated in accordance with the invention, i.e. not having had the treatment referred to above between the water bath and the application of the spin 20 finish, has the following typical properties:

Fibrillation Index 3  
Tenacity 40-42 cN/tex  
Extensibility 13-15%  
Good Dyeability (N.B. all dyeability tests referred 25 to below are simply visual comparisons with untreated fibre.)

In a first series of tests to determine the effect of using the treatment of the invention, a mixture of a commercially available product "Polymer G" from Precision 30 Processes (Textiles) Limited, glyoxal and a cross-linking catalyst was used in the treatment bath. Polymer G is believed to be an aqueous mixture comprising a solution of

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poly(vinylimidazoline) at a concentration of 0.1% by weight and an emulsion of non-ionic polyethylene at a concentration of 1% by weight.

A series of treatment baths was made up as set out in 5 Table 1 below; the concentration referred to is in g/l of the aqueous Polymer G and the glyoxal in the treatment bath. The Fibrillation Index was measured as set out above. The treatment bath also contained a cross linking catalyst for the glyoxal, at a level of 25% of the glyoxal concentration. 10 Typically "Condensol FB" (Trade Mark of BASF AG) was used as the catalyst; this is believed to be a composition of magnesium chloride and zinc fluoroborate.

Table 1

15	Polymer G Concentration	Glyoxal Concentration	Fibrillation Index
Bath 1	0	0	3
Bath 2	10	2	2.2
Bath 3	12	2.4	1.75
Bath 4	15	3	1.4
20 Bath 5	20	4	1.2
Bath 6	25	5	1
Bath 7	30	6	1
Bath 8	40	8	0.8
Bath 9	50	10	0.5

25

The information contained in Table 1 is displayed graphically in Figure 1. It can be seen that the improvement obtained in Fibrillation Index levels out above a concentration of about 20 g/l Polymer G plus 4 g/l 30 glyoxal.

In a further series of baths, Polymer G alone was used as the treatment at varying concentrations. The results of these trials are given in Table II.

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Table II

	Polymer G Concentration g/l	Fibrillation Index
Bath 10	10	2.2
5 Bath 11	20	1.5
Bath 12	30	1.1

These results are also displayed graphically in Figure 1.

Tenacity and extensibility tests were then carried out 10 on the fibres treated with: 10 g/l Polymer G plus 2 g/l glyoxal and 0.5 g/l catalyst; 20 g/l Polymer G plus 4 g/l glyoxal and 1 g/l catalyst; and 30 g/l Polymer G plus 6 g/l glyoxal and 1.2 g/l catalyst. The results of these tests are given in Table III.

15

Table III

	Polymer G Concentration g/l	Tenacity cN/tex	Extensibility %
20 Untreated	0	40-42	13-15
Bath 10	10	39.7	14.7
Bath 11	20	38.2	14.3
Bath 12	30	41.4	15.7

Fibres treated with Polymer G alone at a concentration 25 of 25 g/l had a tenacity of 40.2 cN/tex and an extensibility of 16.4%.

The tenacity and extensibility figures are plotted in Figure 2, and it can be seen that the treatments of the invention give rise to little change in either tenacity or 30 extensibility.

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Visually there was no difference in the dyed colour of the treated fibres at any of the concentrations of Polymer G/glyoxal and catalyst compared to untreated fibre.

As a measure of comfort of the fibre in use, water 5 imbibition tests were carried out. Cotton, normally considered a comfortable fibre, has a water imbibition of 50%. A control sample and the treated fibres of the invention gave the results shown in Table IV:-

10

Table IV

Water Imbibition %

Untreated Fibre	65
20 g/l Polymer G plus	
4 g/l glyoxal and catalyst	59.9
15 40 g/l Polymer G plus	
4 g/l glyoxal and Catalyst	56.5
20 g/l Polymer G	63
40 g/l Polymer G	61.7
Cotton	50

20 It can be seen, therefore, that the invention provides a treatment which reduces fibrillation (which causes pilling of cloth and gives unwanted hairiness to the cloth and unwanted visual effects to cloth made of very fibrillated fibres), whilst not affecting to any significant amount 25 dyeability, tenacity, extensibility or water imbibition.

The properties present in combination in fibre treated by the preferred embodiments of the invention might almost be thought to be mutually exclusive - for example it might be thought that adding a material to the fibre which links 30 into the fibre in some way so as to reduce fibrillation might affect dyeability or extensibility but this has been found not to be true with the method of the invention. Not only are these properties preserved but the fibre is processable into sliver, yarn and fabric. The treatment of 35 the invention is able to do all this and still resist the

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scouring, bleaching and dyeing treatments.

Other suitable compositions for the treatment baths include:

- (1) 1% solids by weight of the fibre of non-ionic polyethylene emulsion (Bradsyn P.E.); 0.1% solids by weight of the fibre of polyelectrolyte ("Primafloc C7", a Trade Mark of Rohm and Haas Limited); at a 30:1 liquor to fibre ratio; at a pH of 5.0 for 15 minutes at 40°C. The pH was adjusted to 5.0 by addition of 10% (w/v) orthophosphoric acid.
- (2) 75 grams solids per litre of non-ionic polyethylene emulsion (Iberlene P.E.); and 1.0 grams solids per litre of polyelectrolyte (Primafloc C7); at 40°C.

Example 13

Cellulose fibre was prepared as described in Example 1. The treatment bath was a 100 g/l solution in water of a polyamide epichlorhydrin resin sold by Hercules Inc. as a 12.5% aqueous solution under the Trade Mark "Hercosett 125". The best results were obtained when the pH of the bath was controlled at about 7.3-7.9. The results at this pH range, in comparison with a control sample, were as follows:

	Control	Hercosett-treated
Fibrillation Index	3.8	1.3
Tenacity cN/tex	42.3	41.2
Extensibility %	14.9	14.5
Water Imbibition %	56	56

Examples 14 and 15

Cellulose fibre was prepared as described in Example 1. The treatment baths used were:

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Bath 14	30 g/l	Polymer VG
	6 g/l	glyoxal
	4 g/l	Consensol FB
Bath 15	30 g/l	Polymer VG

5 "Polymer VG" (Trade Mark) is available from Precision Processes (Textiles) Limited. It is believed to be an aqueous solution of 0.1% by weight poly(vinylimidazoline). The results were as follows:

		Bath 14	Bath 15
10	Fibrillation Index	1.1	1.3
	Tenacity CN/tex	39.2	41.6
	Extensibility %	14.8	14.4

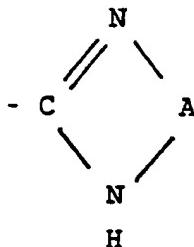
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CLAIMS

1. A method of manufacturing regenerated cellulose fibre with a reduced tendency to fibrillation, characterised in that never-dried regenerated cellulose fibre is treated 5 with an aqueous solution or dispersion of a polymer having a plurality of cationic ionisable sites.

2. A method according to claim 1, characterised in that the polymer has a backbone exclusively of carbon atoms, to which are attached units of the formula:

10



where A is a C<sub>2</sub> to C<sub>3</sub> alkylene group in which different 15 carbon atoms are linked to the two nitrogen atoms.

3. A method according to claim 1, characterised in that at least some of the cationic ionisable sites in the polymer are azetidinium cations.

4. A method according to claim 3, characterised in 20 that the polymer is prepared by condensation of a diacid with a compound containing two primary amine groups and at least one secondary amine group, followed by reaction with an epihalohydrin.

5. A method according to any preceding claim, 25 characterised in that the fibre is so treated as to deposit 0.1 to 0.5 per cent by weight of the polymer on the fibre.

6. A method according to any preceding claim, characterised in that the never-dried fibre is treated in

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addition with an aqueous emulsion of an emulsifiable polymer.

7. A method according to claim 6, characterised in that the aqueous emulsion of the emulsifiable polymer is a 5 non-ionic polymer emulsion.

8. A method according to claim 7, characterised in that the emulsifiable polymer is polyethylene.

9. A method according to any of claims 6 to 8, characterised in that the emulsion contains less than 1 per 10 cent by weight of emulsifiable polymer.

10. A method according to any of claims 6 to 9, characterised in that the pH of the emulsion is in the range 4 to 7.

11. A method according to any of claims 6 to 10, 15 characterised in that the never-dried fibre is treated with a mixture of the polymer having a plurality of cationic ionisable sites and the emulsifiable polymer.

12. A method according to any of claims 6 to 10, characterised in that the never-dried fibre is treated 20 sequentially with the polymer having a plurality of cationic ionisable sites and the emulsifiable polymer.

13. A method according to any of claims 6 to 12, characterised in that the fibre is so treated as to deposit 0.75 to 2.0 per cent by weight of the emulsifiable polymer 25 on the fibre.

14. A method according to any preceding claim, characterised in that the aqueous solution or dispersion of the polymer having a plurality of cationic ionisable sites additionally comprises glyoxal.

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15. A method according to claim 14, characterised in that the aqueous solution or dispersion contains 2 to 10 grams of glyoxal per litre.

16. A method according to any preceding claim, 5 characterised in that the never-dried regenerated cellulose fibre is a solvent-spun fibre prepared by a method including the steps of:

- (i) dissolving cellulose in a water-miscible solvent to form a dope;
- 10 (ii) extruding the dope to form extruded filaments; and
- (iii) passing the extruded filaments into water to remove solvent and form regenerated cellulose fibre.

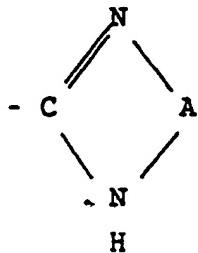
15 17. A method according to claim 16, characterised in that the water-miscible solvent is a tertiary amine N-oxide.

18. A method according to claim 17, characterised in that the solvent is N-methylmorpholine-N-oxide.

19. Regenerated cellulose fibre, characterised in that 20 it bears a coating which comprises a polymer having a plurality of cationic ionisable sites.

20. Fibre according to claim 19, characterised in that the polymer has a backbone exclusively of carbon atoms, to which are attached units of the formula:

25



where A is a C<sub>2</sub> to C<sub>3</sub> alkylene group in which different

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carbon atoms are linked to the two nitrogen atoms.

21. Fibre according to claim 19, characterised in that at least some of the cationic ionisable sites in the polymer are azetidinium cations.

5 22. Fibre according to claim 21, characterised in that the polymer is prepared by condensation of a diacid with a compound containing two primary amine groups and at least one secondary amine group, followed by reaction with an epihalohydrin.

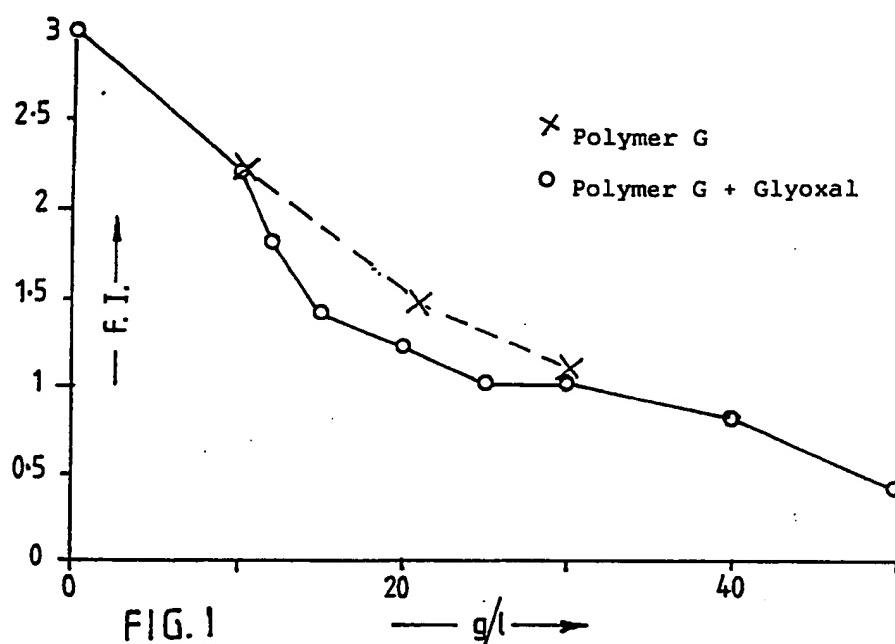
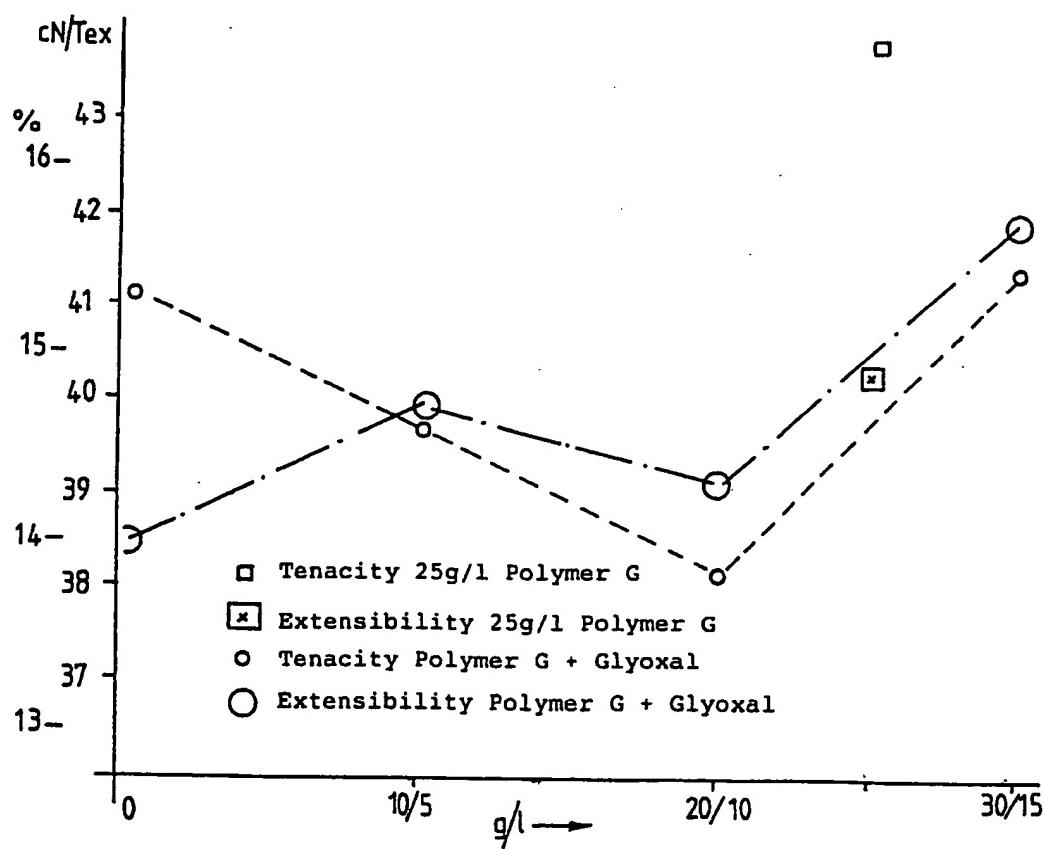
10 23. Fibre according to any of claims 19 to 22, characterised in that the weight of the polymer in the coating is 0.1 to 0.5 per cent, based on the weight of the fibre.

24. Fibre according to any of claims 19 to 23,  
15 characterised in that the coating additionally comprises a polymer which is emulsifiable in water.

25. Fibre according to claim 24, characterised in that at least some of the emulsifiable polymer is polyethylene.

26. Fibre according to claim 24 or 25, characterised  
20 in that the weight of the emulsifiable polymer in the coating is 0.75 to 2.0 per cent, based on the weight of the fibre.

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FIG. 1FIG. 2

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 91/01776

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)<sup>6</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.C1. 5 D01F2/00; D01F11/02; D06M15/356; D06M23/00  
D06M15/39

## II. FIELDS SEARCHED

Minimum Documentation Searched<sup>7</sup>

Classification System	Classification Symbols
Int.C1. 5	D01F ; D06M

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched<sup>8</sup>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>

Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	FR,A,2 450 293 (AKZONA INCORPORATED) 26 September 1980 see page 14, line 1 - line 21; claims & GB,A,2 043 525 8 October 1980 cited in the application ---	1-26
Y	FR,A,1 158 775 (BADISCHE ANILIN- & SODA-FABRIK AG.) 19 June 1958 see the whole document ---	1-26
Y	FR,A,1 148 892 (HOECHST AG.) 17 December 1957 see the whole document ---	1-26
Y	FR,A,2 407 280 (AKZONA INCORPORATED) 25 May 1979 see page 13, line 13 - line 22; claims ---	1-26
		-/-

<sup>10</sup> Special categories of cited documents :<sup>10</sup>

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "A" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

22 JANUARY 1992

Date of Mailing of this International Search Report

18.02.92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

BLAS V.



## III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	<p>WPI, FILE SUPPLIER, DERWENT PUBLICATIONS LTD.,  LONDON, GB;  AN=78-34472A &amp; JP-A-53 035 017 (ASAHI)  1 APRIL 1978  see the whole abstract</p> <p>---</p>	1
A	<p>JOURNAL OF THE TEXTILE INSTITUTE.  vol. 78, no. 5, 1987, MANCHESTER GB  pages 357 - 361;  P. PAVLOV , E. LOZANOV: 'Properties of Viscose Fibres Modified in an As-spun State by Cross-linking.'  see the whole document</p> <p>---</p>	1

**ANNEX TO THE INTERNATIONAL SEARCH REPORT**  
**ON INTERNATIONAL PATENT APPLICATION NO. GB 9101776**  
**SA 52043**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 22/01/92

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
FR-A-2450293	26-09-80	US-A-	4246221	20-01-81
		AT-B-	387792	10-03-89
		AU-A-	4593779	04-09-80
		BE-A-	875323	04-10-79
		CA-A-	1141913	01-03-83
		DE-A,C	2913589	11-09-80
		GB-A,B	2043525	08-10-80
		JP-C-	1308043	13-03-86
		JP-A-	55118928	12-09-80
		JP-B-	60028848	06-07-85
		NL-A-	7902782	04-09-80
		SE-B-	444191	24-03-86
		SE-A-	7902733	03-09-80
		US-A-	4416698	22-11-83
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GB-A-2043525	08-10-80	US-A-	4246221	20-01-81
		AT-B-	387792	10-03-89
		AU-A-	4593779	04-09-80
		BE-A-	875323	04-10-79
		CA-A-	1141913	01-03-83
		DE-A,C	2913589	11-09-80
		FR-A,B	2450293	26-09-80
		JP-C-	1308043	13-03-86
		JP-A-	55118928	12-09-80
		JP-B-	60028848	06-07-85
		NL-A-	7902782	04-09-80
		SE-B-	444191	24-03-86
		SE-A-	7902733	03-09-80
		US-A-	4416698	22-11-83
-----	-----	-----	-----	-----
FR-A-1158775		BE-A-	549624	
		DE-B-	1082004	
		GB-A-	810352	
-----	-----	-----	-----	-----
FR-A-1148892		BE-A-	546198	
		FR-A-	1143949	
-----	-----	-----	-----	-----
FR-A-2407280	25-05-79	AT-B-	365663	10-02-82
		AU-A-	4066878	17-04-80
		BE-A-	871428	20-04-79